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(54) DIFFUSING METALS INTO LOW-CARBON STEEL SHEET

(71) We, COCKERILL - OUGREE-PROVIDENCE ET ESPERANCE-LONGDOZ en abregé COCKERILL, a Belgian Body Corporate of Seraing, B.4100, Belgium, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of magnetic steel sheets.

It is known that certain electrical machines, for example motors, dynamos and transformers, have polar members comprising very tight stacks of fine steel sheets which must have clearly determined magnetic properties among which the magnetic permeability and the electrical resistivity are very important.

Sheets having a high electrical resistivity give stacks which have low losses by Foucault current, thus improving the efficiency of the equipment constructed.

Moreover it is known that wattage losses can be considerably decreased by increasing the content of certain elements, for example silicon or aluminium, in the steel. Such an increase in the content of an element can be obtained by incorporating the said element directly into the bath at the time of producing the steel used to make the sheets. When steel sheets in the form of reels are used, this method requires complex and critical rolling and annealing operations if it is desired to obtain silicon or aluminium contents exceeding 3.5%. With increasing alternating current frequency the losses by Foucault currents become more significant. To reduce these losses to an acceptable level it is necessary to greatly increase the electrical resistivity of the steel sheets and to greatly reduce their thickness.

However, even for silicon contents of the order of 3% it is not possible to obtain sheets with a limited thickness, for example 0.15 mm, by cold rolling without performing a complex and costly cycle of intermediate rolling and annealing operations.

It is possible to obtain steel sheets with a high silicon and/or aluminium content and whose thickness is of the order of 0.10 mm by hot rolling separate sheets into plate form and by this technique to obtain reels of sheet steel. However, the supply of these sheets in plate form leads to high handling costs.

To overcome these difficulties and avoid cold lamination of steel sheets with a silicon content above 3.5% it has been proposed to increase the silicon and/or aluminium content of sheets by cleaning the steel sheet or strip, coating it with a thin layer of a silicon or aluminium group metal, for example silicon, aluminium or germanium, diffusing this metal and finally subjecting the coated steel to thermal treatment under a magnetic field. However, this process requires numerous operations, for example a cleaning stage, as well as complicated installations.

Processes are also known for enriching a sheet with silicon wherein the sheets are subjected to annealing in a furnace in which a protective gas which is non-oxidising and which contains a thermally decomposable silicon compound such as silicon tetrachloride is caused to circulate and then to a homogenisation annealing process.

These gaseous processes require costly and complex installations and involve the circulation of toxic materials such as silicon tetrachloride.

According to yet another process a powder containing silicon is heaped on the surface of a steel sheet with a low carbon content and with a thickness slightly greater than the required thickness. The sheet covered with the powder is heated in a protective atmosphere to cause diffusion, subjected to a cold rolling process to achieve the required thickness and the treatment is finally terminated by an annealing process. This process requires special equipment and involves a large number of phases and is therefore highly complicated.

There is thus a need for a simple, safe and economic process for increasing the content

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of the silicon or aluminium group metal of steel sheets of final thickness for example of about 0.10 mm, which eliminates or reduces the difficulties encountered in the known processes and wherein the steel sheet may be obtained in a single rolling phase without intermediate annealing.

According to one feature of the present invention there is provided a process for the manufacture of magnetic steel sheets containing a deposit metal comprising a metal from group III or group IV of the Periodic Table which comprises applying to a soft steel having a carbon content below 0.010% by weight a coating of a paste comprising the deposit metal or an alloy thereof, an inert refractory material, an activating material comprising a halide, and a binder which is volatile without leaving a carbon deposit at the annealing temperature of the steel, drying the coating and then annealing the coated sheet under a reducing atmosphere at a temperature and for a time sufficient to increase the deposit metal content of the sheet.

In general the paste may contain from 2 to 50% by weight of the deposit metal. The paste preferably contains a deposit metal content of 2 to 35% by weight, an inert refractory material content of 65 to 98% by weight and an activating material content of 0.05 to 2% by weight calculated on the basis of the total weight of the dry materials.

The deposit metal contained in the paste is preferably added in the form of a powder of particle size about 50 μ . Advantageously the deposit metal is silicon in the form of pure metal or ferrosilicon. The silicon used is preferably added in the form of a powder containing 98 to 99% of pure silicon or, if it is desired to use ferro-silicon this has a silicon content of from 45 to 85% by weight and preferably about 60%.

The inert refractory material is used as a mechanical diluent so as to permit good dispersion of the deposit metal and good circulation of gaseous materials between coil turns during annealing. The inert refractory material is preferably an oxide based on alumina or an aluminosilicate, such as kaolin. Prior to its utilisation it is advantageously calcined to about 1100°C, then ground to a particle size of from 1 to 80 μ . Alumina which has been treated in this way has the advantage of not absorbing water of crystallization.

As the activating agent a substance which liberates halogen or a hydrogen halide on heating and preferably which does not give off dangerous or unpleasant vapours at ambient temperature can be used. Suitable activating materials include halides of iron, silicon, aluminium and ammonium preferably ammonium iodide or ammonium chloride.

In the case where the deposit metal is silicon it is possible to add silicon iodide to the

mixture formed with the inert material which eliminates the need for further activating materials. However, in practice it is more advantageous to use ammonium iodide and to form SiI_4 in the mixture by heating the mixture containing the silicon metal based powder, the alumina base material and NH_4I at a temperature of about 1050°C prior to the formation of the paste or during the temperature rise of the paste-coated sheet.

The deposit metal based mixture, the inert material and the activating agent are formed into a paste, e.g. by addition of water. A binder is added to the liquid to ensure that the said paste adheres well when applied to the sheet. This binder which must be volatile at the annealing temperature must not leave a carbon deposit during its decomposition during annealing.

Among the binders which can be used are in particular polyvinyl alcohols. In practice a polyvinyl alcohol sold under the registered Trade Mark "Rhodoviol" is advantageously used and is added in an amount of 5g/l of water.

The coated sheet is generally annealed at a temperature of from 950 to 1250°C, preferably about 1050°C.

The practical application of the process according to the invention is simple and does not require complex apparatus or installation or the careful handling of dangerous products.

Steel sheets of the desired final thickness, and desirably having contents of C, S, P and N as low as possible may be used. Decarbonised steel sheets having a carbon content below 0.010% and preferably below 0.005%, a P content below 0.050% and a S content below 0.015% are suitable. The group III or group IV metals, e.g. silicon or aluminium, can be present in their usual amounts, generally below 1%.

A temporary coating of the aqueous paste containing the deposit metal, the inert refractory material, the activating material and the binder in the form of an adhesive and porous layer is applied to the sheet which has been brushed and from which the surface oxides have been removed, and after drying the coated sheet is annealed.

The following Examples serve to illustrate the process of the present invention.

Example 1

A dry mixture containing 2 kg of Al_2O_3 having a particle size of about 80 μ , 1 kg of ferrosilicon in the form of fine powder of particle size about 60 μ and having a silicon content of about 75% and 4 g of NH_4I in the solid state to facilitate manipulation was prepared.

This dry mixture was heated to a temperature of 1050°C for 24 hours and was then added to 1200 cc of water, wherein had pre-

viously been introduced 6 g of a polyalcohol sold under the Trade Mark "Rhodoviol".

In this way an aqueous paste was obtained which was applied with a spray gun to form a coating on the surface of a steel sheet which was 0.35 mm thick and whereof the carbon content was 0.003% whilst the silicon content was approximately the same as the content of residual impurities in the steel.

The quantity of paste deposited was such that about 142 g of silicon were deposited per m² of sheet. The coated sheets were then heated at a temperature of about 250°C for a short time so as to dry the coating, stacked and subjected to annealing at a temperature of about 1050°C for a period of 24 hours under a protective atmosphere containing in particular dry hydrogen. In this way magnetic steel sheets having a silicon content of about 3.5% were finally obtained. The silicon was distributed uniformly throughout the thickness of the sheet.

Example 2

As in Example 1 a paste was prepared which was supplied by spray gun to sheets identical to those of Example 1. The thickness of paste was such that about 190 g of silicon were deposited per m² of sheet surface.

After receiving the coating the sheets were first heated at about 250°C for a short time to dry them and then annealed at 1050°C for 24 hours in a reducing atmosphere of dry hydrogen.

In the sheets thus obtained the silicon was uniformly distributed and had a content of 5%.

Example 3

As in Example 1 a paste was prepared which was applied with a spray gun to sheets identical to those of Example 1. The thickness of paste applied was such that about 185 g of silicon was deposited per m² of sheet surface.

After drying the coating as in Example 1 and 2, the sheets were stacked and were subjected to annealing at 1050°C for a period of 32 hours in a dry hydrogen atmosphere.

In the sheets thus obtained the silicon was uniformly distributed and had a content of 4.85%.

The sheets which were 0.4 mm thick possessed the following magnetic properties when measured on the Epstein frame: at 1 Tesla and 50 Hz the losses were found to be equal to 1 W/kg; at 1.5 Tesla and 50 Hz the losses were 2.37 W/kg. The induction obtained at 10 Oe was 1.32 Tesla.

The sheets were then heated to 650°C and immediately cooled whilst being subjected to the action of a 100 Oe magnetic field. The following results were then obtained: at 1 Tesla and 50 Hz the losses were below 0.9

W/kg and at 1.5 Tesla and 50 Hz the losses were 2.33 W/kg.

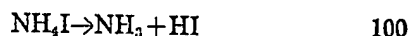
The proportion of dry material to be incorporated in the water to form the paste was varied according to the method used for the application. If the quantity of material was too large the paste was not wet enough and could not be applied easily and did not stick suitably to the sheet. If the quantity of material was too low the paste was too fluid and it dripped when the coated sheet was moved.

The weight of paste to be deposited on the sheet varied and depended in particular on the thickness of the sheets to be treated and on the final deposit metal content required.

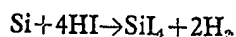
When operating in the manner described hereinbefore, particularly in the Examples, we have found that the coating formed by the dried paste on the sheet adhered strongly. This was advantageous during the stacking of the sheets in plate form and when winding the sheet onto a reel in the form of a band which was wound so that the coating was located towards the inside of the turns.

Thus it was unnecessary to compact the coating. The sheets which were stacked or wound onto reels were then subjected to heating in a furnace in a protecting atmosphere which did not contain C, N₂ or O₂, but which did contain dry H₂. The temperature was progressively raised until a temperature of about 1050°C was attained. This temperature was maintained for a period of about 40 hours.

When the heating temperature reaches 250°C the ammonium iodide of the coating decomposes according to the reaction:

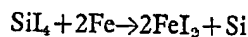


Then, the silicon contained in the ferrosilicon undergoes the following reaction:

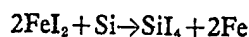


The production of hydrogen during this reaction contributes to the maintenance of the reducing atmosphere which is advantageous.

Above about 290°C SiI₄ which is gaseous moves by convection towards the surface of the sheet where the following reaction takes place:



The silicon thus produced diffuses into the sheet and increases the silicon content thereof. Moreover FeI₂ which is also a gas at the treatment temperature moves by convection within the sheet where it reacts with the silicon according to the reaction:



As a result the sheet is enriched with sili-

con whilst the coating becomes equivalently deficient in this element. At the end of a particular time an equilibrium is established which depends on the quantity of silicon and iron contained in the coating and the temperature at which the annealing is performed.

The annealing temperature which is generally between 950 and 1250°C, preferably 1050°C, is maintained for a period sufficient to ensure that the silicon deposited is distributed in a uniform manner throughout the sheet. This period which varies according to the thickness of the sheet and according to the quantity of the silicon to be deposited is from 8 to 70 hours.

The manufacturing process according to the invention is simple because the decarbonised steel sheet does not undergo any size change during treatment and need undergo no prior preparation.

The process is performed on materials which are not dangerous, toxic, nor unpleasant to handle and to perform the treatment it is not necessary to introduce dangerous gases from external sources. The paste may be conveniently applied by simple techniques such as a brush or spray gun, in such a way that no complicated equipment is necessary.

Finally the process provides for the production in an economic manner of sheets having a high silicon content and in particular of sheets which a high silicon content and with very low thicknesses and produced in reel form. This is possible since rolling of the sheets is effected prior to the incorporation of the silicon thus avoiding the complex and costly cycle of rolling and annealing operations or hot rolling of stacks of sheets or plates of reduced length previously used.

WHAT WE CLAIM IS:—

1. A process for the manufacture of magnetic steel sheets containing a deposit metal comprising a metal from group III or group IV of the Periodic Table which comprises applying to a soft steel sheet having a carbon content below 0.010% by weight a coating of a paste comprising the deposit metal or an alloy thereof, an inert refractory material, an activating material comprising a halide, and a binder which is volatile without leaving a carbon deposit at the annealing temperature of the steel drying the coating and then annealing the coated sheet under a reducing atmosphere at a temperature and for a time sufficient to increase the deposit metal content of the sheet.

2. A process as claimed in claim 1 wherein the soft steel sheet has a carbon content below 0.005% by weight.

3. A process as claimed in claim 1 or claim 2 wherein the paste contains from 2 to 35% by weight of the deposit metal, from 65 to 98% by weight of the inert refractory material and from 0.05 to 2% by weight of

the activating material calculated on the basis of the total weight of dry materials.

4. A process as claimed in any of claims 1 to 3 wherein the deposit metal is added in the form of a powder of particle size about 50 μ .

5. A process as claimed in any of the preceding claims wherein the deposit metal is silicon.

6. A process as claimed in claim 5 wherein the silicon is added in the form of the pure metal or as ferrosilicon.

7. A process as claimed in claim 6 wherein the silicon metal is added in the form of a powder containing from 98 to 99% by weight of pure silicon.

8. A process as claimed in claim 6 wherein the ferrosilicon has a silicon content of from 45 to 85% by weight.

9. A process as claimed in claim 8 wherein the ferrosilicon has a silicon content of about 60% by weight.

10. A process as claimed in any of the preceding claims wherein the inert refractory material comprises an oxide based on alumina or an aluminosilicate.

11. A process as claimed in claim 10 wherein the refractory material comprises kaolin.

12. A process as claimed in claim 10 or claim 11 wherein prior to its use the refractory material is calcined at about 1100°C and then ground to a powder with a particle size from 1 to 80 μ .

13. A process as claimed in any of the preceding claims wherein the activating material comprises a substance which liberates halogen or a hydrogen halide on heating.

14. A process as claimed in claim 13 wherein the activating material comprises an iron, silicon, aluminium or ammonium halide.

15. A process as claimed in claim 14 wherein the activating material comprises ammonium iodide or ammonium chloride.

16. A process as claimed in any of the preceding claims wherein the binder is a polyvinyl alcohol.

17. A process as claimed in any of the preceding claims wherein the paste is an aqueous paste.

18. A process as claimed in any of the preceding claims wherein the coated sheet is annealed at a temperature of from 950 to 1250°C.

19. A process as claimed in claim 18 wherein the coated sheet is annealed at a temperature of about 1050°C.

20. A modification of a process as claimed in any of the preceding claims wherein the paste comprises silicon iodide, the inert refractory material and the binder.

21. A process as claimed in claim 1 substantially as herein described.

22. A process as claimed in claim 1 substantially as herein described with reference to the Examples.

23. A magnetic steel sheet containing a deposit metal of the silicon or aluminium group whenever produced by a process as claimed in any of claims 1 to 22.

- 5 24. A magnetic steel sheet as claimed in claim 23 with a thickness of about 0.10 mm.

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